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Further studies on zirconia gels

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FURTHER STUDIES ON ZIRCONIA GELS

by

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By J. E. Anderson

Approved by J. J. Porter

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Introduction

When solutions of zirconium oxychloride and sodium acetate are mixed at room temperature (25°C.), a grey-white hydrogel of zirconia is formed. This gel structure gradually weakens on standing, and finally becomes a water-clear sol. Heating this sol to 60°C. will form a similar gel, stable at this temperature, which will reliquefy on cooling to 25°C. The gelation-reliquefaction cycle can apparently be carried out indefinitely.

Such behavior is in direct contrast to normal gelation. The so-called "irreversible gels", such as those of silicic acid, show stability at all temperatures; while other "reversible gels", such as common gelatin, set at lower temperatures and become liquid on heating. McBain (1) mentions certain organic gels, such as those of methyl cellulose in water and cellulose nitrate in alcohol, which set on heating and liquefy on cooling. Such gels do not, however, first set and then reliquefy at room temperature.

There have been several previous studies seeking to determine the various ionic changes and interactions that govern this unique behavior. Unfortunately, these theories have not been substantiated by experimental findings.

The present study is primarily concerned with a qualitative explanation of the phenomenon; i.e., the basis for gelation and reliquefaction in broad terms. When this has been accomplished, it would then seem proper to contrue a reaction mechanism.

The Aqueous Chemistry of Zirconium

Venable's monograph Zirconium (2) is the recognized comprehensive treatise on this element. Published in 1922, it does not include the later discoveries made by Connick and McVey (3) relating to aqueous solutions. Using the organic complexing agent thenoyltrifluoroacetone, which is soluble in benzene, but insoluble in water, they were able to determine the degree of hydration of the zirconium ion at various acidities, using partition coefficients.

As a result of their investigations, it is now known that (a) even in such strongly acid media as 2 N perchloric acid, the zirconium ion is hydrated to a form between Zr^{++} and $ZrOH^{+3}$; (b) increasing the pH of the solution increases the degree of hydration, until the insoluble hydrated oxide or "hydroxide" is precipitated; (c) this insoluble oxide, ZrO_2, is stable with increasing pH until a very basic solution, pH 14, is reached, where it slowly dissolves to form an hydroxyl complex; (d) the various ionic species tend to polymerize at higher concentrations of zirconium, forming micellular sol particles.

Histppical

Although gels of zirconia have been known since the work of Biltz (4) in 1902, the reliquefaction phenomenon was first reported by Hurd, Fallon, and Hobday (5) in 1942. It appears that the action of acetate upon gelation is unique. Fallon (6) prepared gels from zirconium oxychloride by mixing with solutions of sodium carbonate as well as sodium acetate. The gels made with acetate reliquefied; those prepared with carbonate did not. The energy of activation for gelation was found the same in both cases, 29,000 cal./mol.deg.

Hobday (7) measured the times of set and of reliquefaction as a function of the pH of the mixed solution. His results, which contribute greatly to my explanation of the gel behavior, are plotted in Curve #1.

Kiely (8) concerned himself primarily with the effects of added electrolytes and non-electrolytes to the reaction mixture. He determined that the sol particles of zirconia, like those of other hydrated-oxide sols, were positively charged.

Preparation of Standard Solutions

Following the method of Kiely (8), a standard stock solution of zirconium oxychloride was prepared by dissolving 744 grams of $ZrOCl_2 \cdot 8\ H_2O$ in de-ionized water, and diluting

to two liters. A gravimetric analysis of this solution was made, following the method of Scott (9), using cupferron. The solution was found to be 1.08 molar in ZrO_2.

202 grams of C.P. sodium acetate ($NaC_2H_3O_2 \cdot 3\ H_2O$) was dissolved in enough de-ionized water to make one liter of solution. The resulting molarity was 1.49.

Zirconium oxychloride hydrolyzes in water by the reaction:

$$ZrOCl_2 + n\ H_2O \longrightarrow ZrO(OH)_nCl_{2-n} + n\ H^+ + n\ Cl^-$$

where $n = 0,1,2$

This results in a very acid solution: the oxychloride standard was found to have a pH of 0.5. Sodium acetate, the salt of a strong base and a weak acid, was found to give a solution having a pH of 7.9. A glass electrode apparatus (pH meter) was used in these determinations.

Experimental Procedure

Gels were prepared in 15 x 150 mm. test tubes. In all trials, the acetate was added to the oxychloride; the tube was corked, inverted twice, and allowed to stand. The time of set was defined as the time interval between the beginning of the mixing process and the point where the rigidity of the gel was great enough to permit inversion of the test tube without the gel falling from the bottom. (Flemming's Test Tube Method) With some experience, results can be reproduced with fair precision. Kiely (8) reports agreement within 3 %. The gels never attain the rigidity of the more familiar silicic acid gels, and even in their most rigid form cannot support a glass rod.

Experimental Results

The stock solution of zirconium oxychloride was yellow in color. This fact suggested the possibility of an absorption maximum in the wavelengths of visible light. Absorption studies in this range were made using a Beckman Model DU Spectrophotometer, with de-ionized water serving as the reference sample. The results of these studies are tabulated in Table I, and plotted in Curve # 2. A peak of maximum absorption was found at 335 mμ for the stock oxychloride solution. This peak was absent in the spectrum of the reliquefied sol. Sodium acetate was found to give no appreciable absorption in these wavelengths.

"The absorption of radiant energy in the visible and ultraviolet regions of the electromagnetic spectrum is associated with certain electronic transitions in the absorbing molecule. Specifically, it is believed that the energy of the absorbed radiation causes excitation of outer or valence electrons of the absorbing molecule to orbitals of higher energy than are normally occupied in the ground state. According to an equation developed by Bohr, the difference in energy between the ground and excited state orbitals is proportional to the frequency of the radiation absorbed."(10)

From the preceding discussion, it would seem that there must exist at least two different ionic species (or ionic groupings, if there has been polymerization), before and after gelation: outer electrons may jump to higher energy orbitals in the oxychloride standard, which are filled , and thus unavailable, in the latter case.

There would seem to be three factors that might produce such a change: (a) The rise in pH of the mixture with the addition of acetate, a base. (b) The effect of the acetate ion itself. (c) The effect of un-ionized acetic acid. Trials upon the effect of acetic acid were next carried out.

One milliliter of the stock zirconium oxychloride was diluted with varying concentrations of 1.00 M acetic acid. Spectral data were taken and compiled in Table II. Curve #3 is a plot of these data. From the shape of these curves, which have essentially the same form as the oxychloride standard, it appears that it is not the un-ionized acetic acid that is responsible for the disappearance of the absorption maximum.

The succeeding trials were performed in a similar manner, substituting sodium acetate solution for the acid. Curve #3 shows that at low concentrations of the acetate, there is little absorption change in the oxychloride spectrum. As the mole ratio of acetate to oxychloride becomes greater than one, however, the spectrum assumes a shape similar to that of the reliquefied sol. The addition of acetate, a base,

to the acidic oxychloride also raises the pH of the solution. On the basis of these absorption studies, therefore, it is impossible to tell which of the effects is responsible for the ionic change.

In none of the trials with the various amounts of acetate was there a gel formed; yet, the shift in light absorption occurred. This is a clear indication that the ionic change takes place before, rather than during or after the gel has formed. This corresponds to the "first", or "transitory" sol referred to by Kiely.(11)

At this point, it will be well to consider Hobday's plot of time of set and time of reliquefaction as a function of pH (Curve #1). The first striking feature of the two graphs is the location of a maximum in the reliquefaction curve at the same pH as the minimum for the time of set. The inverse relationship, that those gels which set fastest take longest to reliquefy, is violated only at higher pH; i.e., at higher acetate concentrations. It is also important to note that at these higher acetate concentrations, the pH change per milliliter added acetate is decreasing rapidly: between volumes of 15 and 17 ml., this change is 0.14 pH units/ml.; between 23 and 25 ml., 0.05 pH units/ml.; and between 27 and 29 ml., 0.03 pH units/ml. This decrease is to be expected, since the pH of the sodium acetate-acetic acid buffer is being approached. Since the time of set levels off in this region, it suggests that gelation is directly related to pH. Conversely, since the reliquefaction curve steadily decreases with acetate addition,

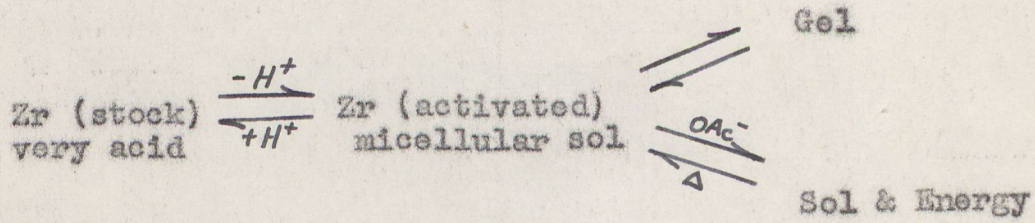
it follows

it follows that it is the acetate concentration that is responsible for this phenomenon.

If a rise in pH is able to cause a shift from one molecular species to another, it was likely that acid addition to the reliquefied sol might reproduce the original ionic form. Curve # 5 illustrates spectra obtained when samples of the sol, at pH 4.4, were diluted with small quantities of perchloric acid. This acid was chosen for two reasons: (a) It is the only strong acid which neither shows absorption in the wavelength range under study, nor has an anion which might attack the sol (to form a precipitate or complex). (b) The acid shows little tendency to form any type of complex in aqueous solution. Curve # 6 shows the absorption spectra of perchloric and nitric acids.

As greater amounts of perchloric acid were added, the zirconium spectrum slowly changed from a shape similar to the reliquefied sol to one like the oxychloride standard. This was further evidence for the relationship between gelation and rise in pH.

With this evidence, it is possible to construct a schematic diagram for the phenomenon:



It is hypothesized that the initial rise in pH of the zirconium oxychloride shifts the various ionic equilibria present in the favor of some reactive micellular species. When the concentration of this micelle reaches some limit, a gel is formed. This is borne out by the initial decrease in the time of set in Curve #1. After some pH (about pH 4.35), formation of this reactive micelle is no longer favored by the several equilibria, and the time of set increases until the buffered solution is reached.

This reactive species is acted upon by the acetate, at a slower rate, to form a sol. It is strongly indicated that energy, probably in the form of heat is liberated as this second, unreactive sol is formed: it is observed that heating this second sol will cause a gel to be formed. This amounts to reversing the path of this chemical equilibrium.

Tests on this hypothesis were made. Efforts were made to determine whether gels might be preserved without any reliquefaction at room temperature, if the acetate ion concentration were very low. It was found that if 0.5 ml. of the oxychloride standard was mixed with 0.5 ml. of 2.14 M sodium acetate, then diluted to 10 ml. with de-ionized water, gels could be formed which would not reliquefy. The pH of these gels was 6.3. Curve #7 illustrates the three regions where different products are formed. Admittedly, there are far from enough data plotted; yet, it can be seen that no gel will form when the oxychloride concentration is "high", and the acetate is "low"; reliquefaction will occur in cases where both are "high"; and a stable gel results when both are "low".

A second series of experiments were run. This time the reliquefied sol was diluted to twice, and to four times its original volume. On standing overnight, both diluted solutions had become opaque, and after one week, a soft gel had formed in the tube having the greatest dilution. Dilution of the sol in a similar manner, using 2.14 M sodium acetate solution rather than de-ionized water produced a similar effect. Since this could have been produced by the further rise in pH with dilution, a third set of trials was made, using a buffered solution of sodium acetate and acetic acid (pH 3.8). This time no tendency to form a gel was noted after two weeks.

Removal of the acetate ion from the reliquefied sol was attempted by dialysis of the sol against a surrounding vessel of de-ionized water, through a collodion membrane. A soft gel was formed within the membrane overnight. When a solution of concentrated sodium acetate was substituted for the water, the sol within the membrane was still liquid after two days, but set to a gel after a week. In this case too, there is the possibility of a secondary effect due to further rise in pH.

An interesting phenomenon is illustrated by Curve #6. A limited amount of acetate, which was not enough to cause gelation, was added to a fixed amount of the oxychloride. After a measured time interval had elapsed, a second portion of acetate was added. This too, would have been insufficient

to cause gelation by itself, but the total amount was great enough to form a gel that would reliquefy. The time of set was measured from the initial mixing of acetate. The curve shows that the time of set varies almost linearly with this delay interval.

At first glance, it might appear that the delay in set was due entirely to the delay in acetate addition. However, it is apparent on closer scrutiny that while the gel formed by mixing both portions of acetate at once with the oxychloride set in 1.45 minutes (time: t=0), that formed after a three minute delay took 11.75 minutes to set, or 8.75 minutes after the second addition of acetate. Other values are given in Table V .

This phenomenon can also be explained by the assumed hypothesis. At all times, the gelation and peptization processes are in competition. Before any gel is formed, the reactive micelle is interacting with acetate ion to form a stable sol. The longer the time lapse between additions of acetate, the more of this micelle will be converted, and thereby incapable of gelation. When the second portion of acetate is added, the pH is raised again, more of the micelle is formed, but the instantaneous concentration of the micelle (the critical factor in gelation), will be less than before. If several hours pass between the two additions, one can pass from the stock oxychloride to the form of the reliquefied sol without a gel being formed. This sol will exhibit all the properties of the sol that had first gelled.

Summary

A study was made on the unique behavior of certain gels of zirconia which first set and then liquefy at room temperature. Using absorption measurements in the visible range of the light spectrum, it was demonstrated that this behavior was the result of two competing reactions. Gelation was found to be caused by the rise in pH that accompanied mixing of solutions of sodium acetate and zirconium oxychloride. The reliquefaction process, or the destruction of the gel structure, was found to be dependent upon the concentration of acetate ion present.

No evidence was found to support a reaction mechanism. At best, there is known to be some shift from the initial acidic form of the zirconium ion to a second, micellar species, but neither have been determined.

Weiser (12) states that "highly dispersed particles that adsorb water strongly are of primary importance for the formation of hydrous jellies..." From this, it would seem that the micellar species,formed by the rise in pH, must be strongly hydrophillic.

There are several theories as to how sol particles are hydrated, and how such hydrated micelles unite to form gels. A familiar interpretation is given by Kruyt and van Klooster (13) who suggest a "sponge" system, with both liquid and solid

phases continuous. Whatever the actual gel structure, it is evident that the acetate ion must somehow rupture the bonds between the individual micelles,and form a stable sol. The observed regelation at higher temperatures may be due to an increased micelle-micelle attraction, decreased peptization ability of the acetate, or a combination of the two.

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Acknowledgments

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Table I

Spectra of the Reactants

Wavelengths in mμ	Optical Density		
	0.22 M $ZrOCl_2$	1.2 M $NaC_2H_3O_2$	Reliquefied Sol
230	infinite	2.0	infinite
235	infinite	0.850	infinite
240	infinite	0.227	infinite
245	infinite	0.048	infinite
280	0.565	no absorption	1.70
285	0.461	in this region	1.80
290	0.385		1.53
295	0.356		1.33
300	0.356		1.28
305	0.364		0.970
310	0.402		0.820
315	0.448		0.685
320	0.487		0.585
325	0.530		0.505
330	0.550		0.413
335	0.555		0.336
340	0.550		0.267
345	0.518		0.220
350	0.473		0.165
355	0.418		0.127
360	0.355		0.108

Table II

Effect of Acetic Acid

Wavelength in mμ	Optical Density		
	0.07 M	0.21 M	0.78 M
280	-	1.20	1.55
285	-	0.950	1.25
290	-	0.745	0.990
295	1.80	0.610	0.785
300	1.13	0.535	0.665
305	0.780	0.525	0.615
310	0.648	0.555	0.630
315	0.630	0.600	0.675
320	0.651	0.650	0.730
325	0.705	0.710	0.790
330	0.730	0.745	0.820
335	0.740	0.750	0.830
340	0.715	0.740	0.820
345	0.675	0.695	0.780
350	0.619	0.640	0.720
355	0.555	0.565	0.640
360	0.475	0.486	0.558

Table III

Effect of Acetate on Spectra

(All trials 0.24 M. in $ZrOCl_2$)

Wavelengths in mμ	Optical Density 0.12 M NaAc pH 2.1	0.23 M NaAc pH 2.2	0.35 M NaAc pH 2.6	0.47 M NaAc pH 4.1
280	1.24	1.23	1.90	infinite
285	0.98	1.01	1.80	infinite
290	0.780	0.810	1.50	1.80
295	0.645	0.672	1.29	1.55
300	0.580	0.590	1.10	1.34
305	0.568	0.559	0.95	1.12
310	0.593	0.568	0.820	0.96
315	0.650	0.597	0.720	0.780
320	0.715	0.635	0.615	0.640
325	0.750	0.671	0.537	0.520
330	0.790	0.691	0.472	0.406
335	0.802	0.688	0.415	0.324
340	0.790	0.675	0.355	0.250
345	0.745	0.630	0.305	0.190
350	0.681	0.571	0.263	0.145
355	0.605	0.510	0.225	0.115
360	0.519	0.440	0.186	0.082

Table IV

Reliquefied Sol as a Function of pH

Sol: 0.22 M in $ZrOCl_2$
0.90 M in $NaC_2H_3O_2$

Acid: concentrated perchloric

Wavelengths in mμ	Optical Density pH 4.4	pH 3.5	pH 2.8	pH 1.9	pH 1.1
300	1.08	0.790	0.571	0.538	0.380
305	0.92	0.560	0.375	0.343	0.260
310	0.795	0.405	0.282	0.250	0.210
315	0.680	0.314	0.250	0.216	0.195
320	0.565	0.260	0.245	0.225	0.210
325	0.470	0.210	0.245	0.230	0.223
330	0.386	0.166	0.245	0.230	0.230
335	0.306	0.129	0.240	0.227	0.228
340	0.243	0.106	0.225	0.225	0.221
345	0.188	0.080	0.209	0.210	0.215
350	0.143	0.061	0.192	0.190	0.198
355	0.107	0.046	0.167	0.168	0.170
360	0.079	0.034	0.142	0.144	0.146

Table V

Delay in Addition of Acetate

(Data in Minutes)

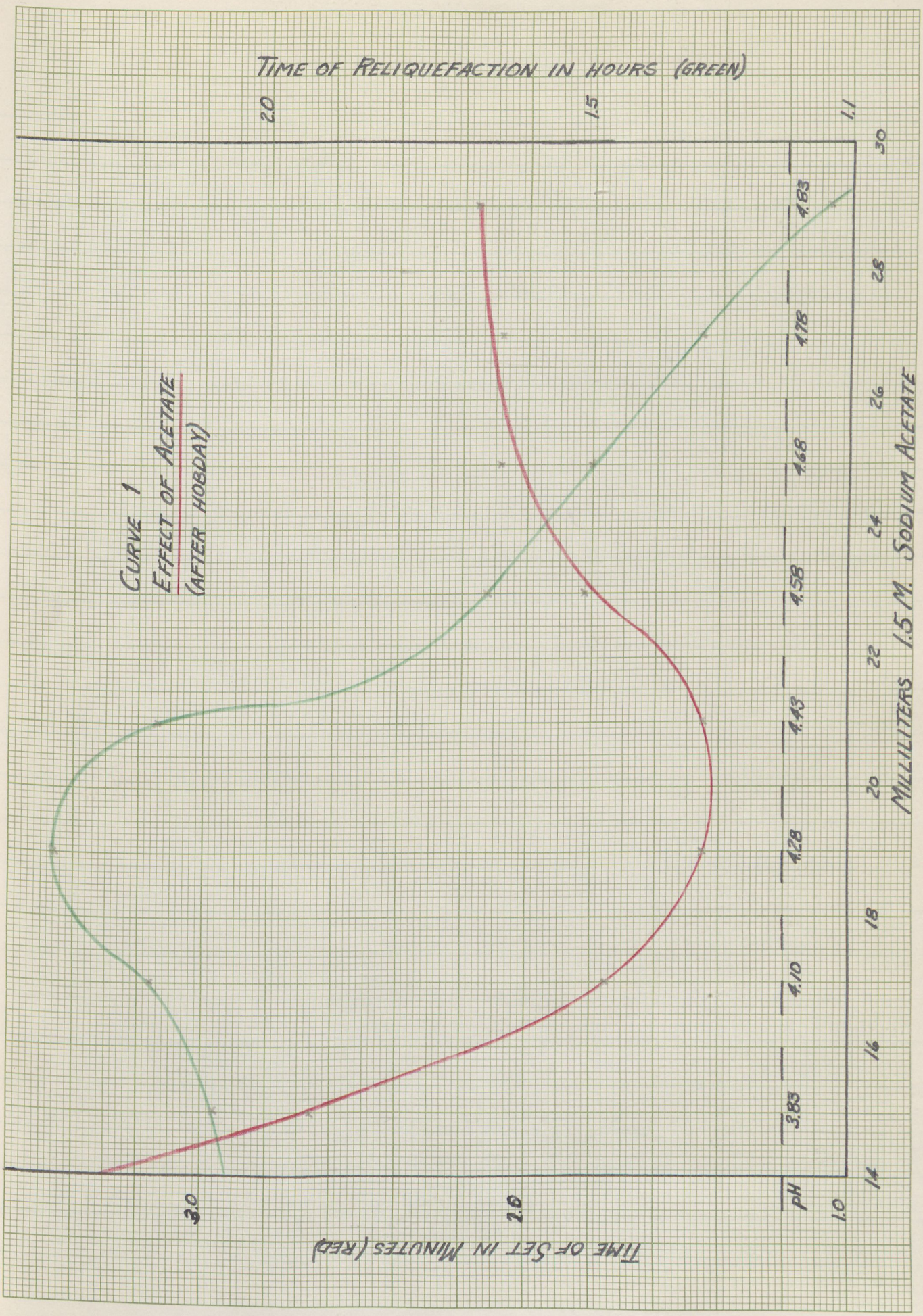
Delay Interval	Time of Set	Time After 2nd Addition	Reference * Interval
0:00	1:45	1:45	0:00
0:30	2:45	2:15	0:30
1:00	4:15	3:15	1:30
1:30	6:00	4:30	2:45
2:00			
2:30	7:15	4:45	3:00
3:00	11:45	8:45	7:00
3:30	11:15	7:45	6:00
4:00	13:00	9:00	7:15
4:30	17:00	12:30	10:45

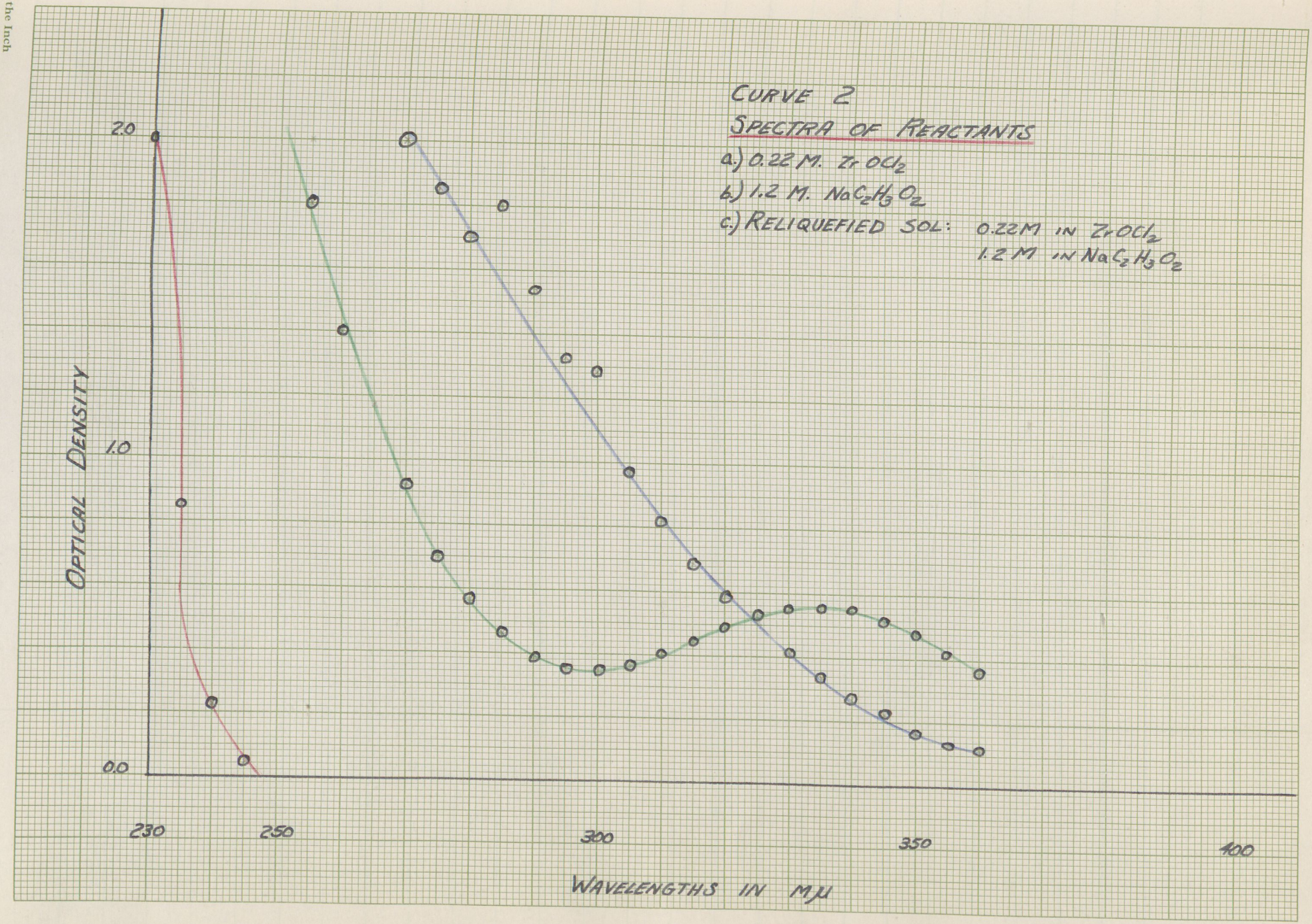
* The reference interval is the difference between the "Time After 2nd Addition" and the "time of set" of the gel in which the two portions of acetate were added together.

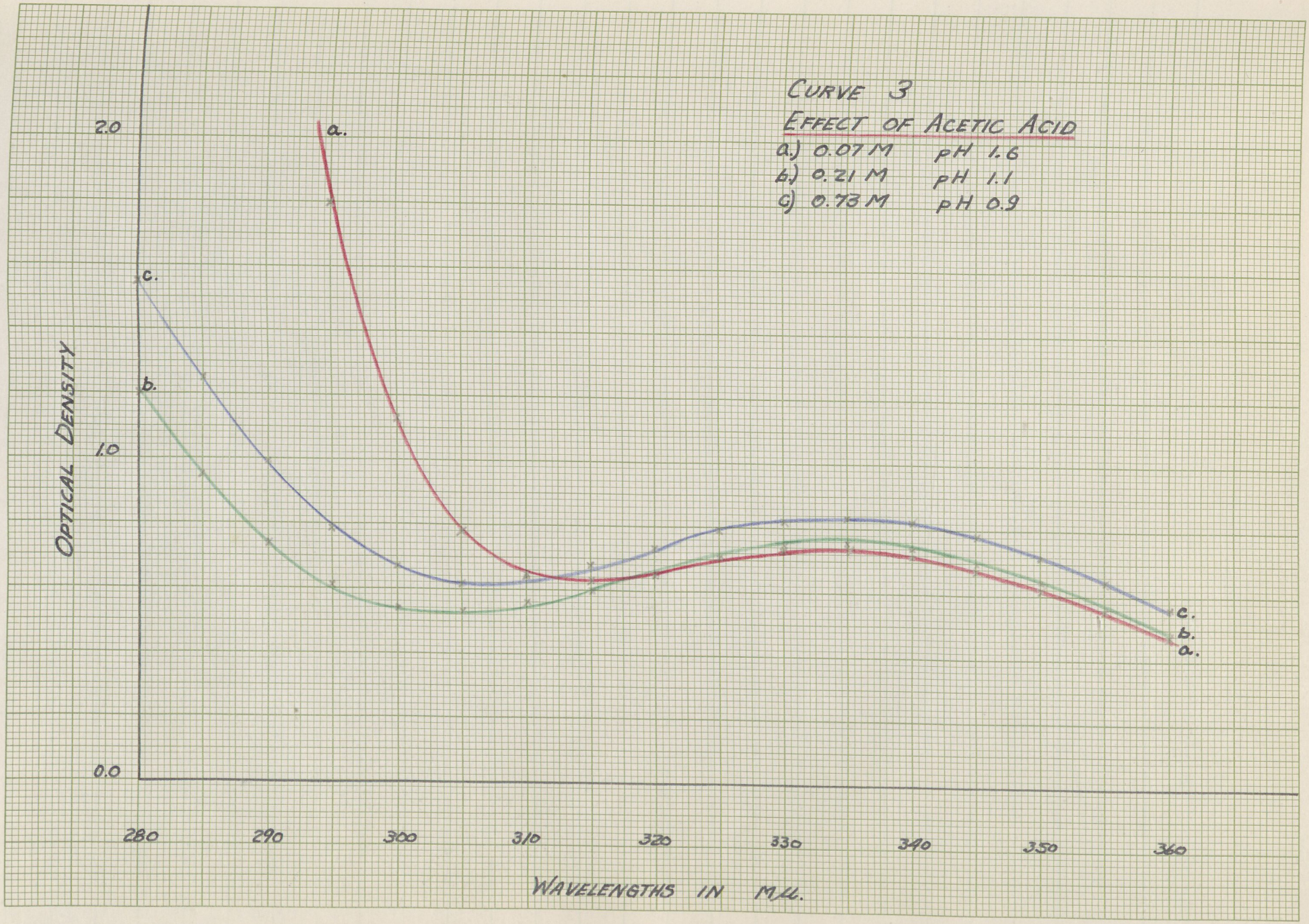
Table VI

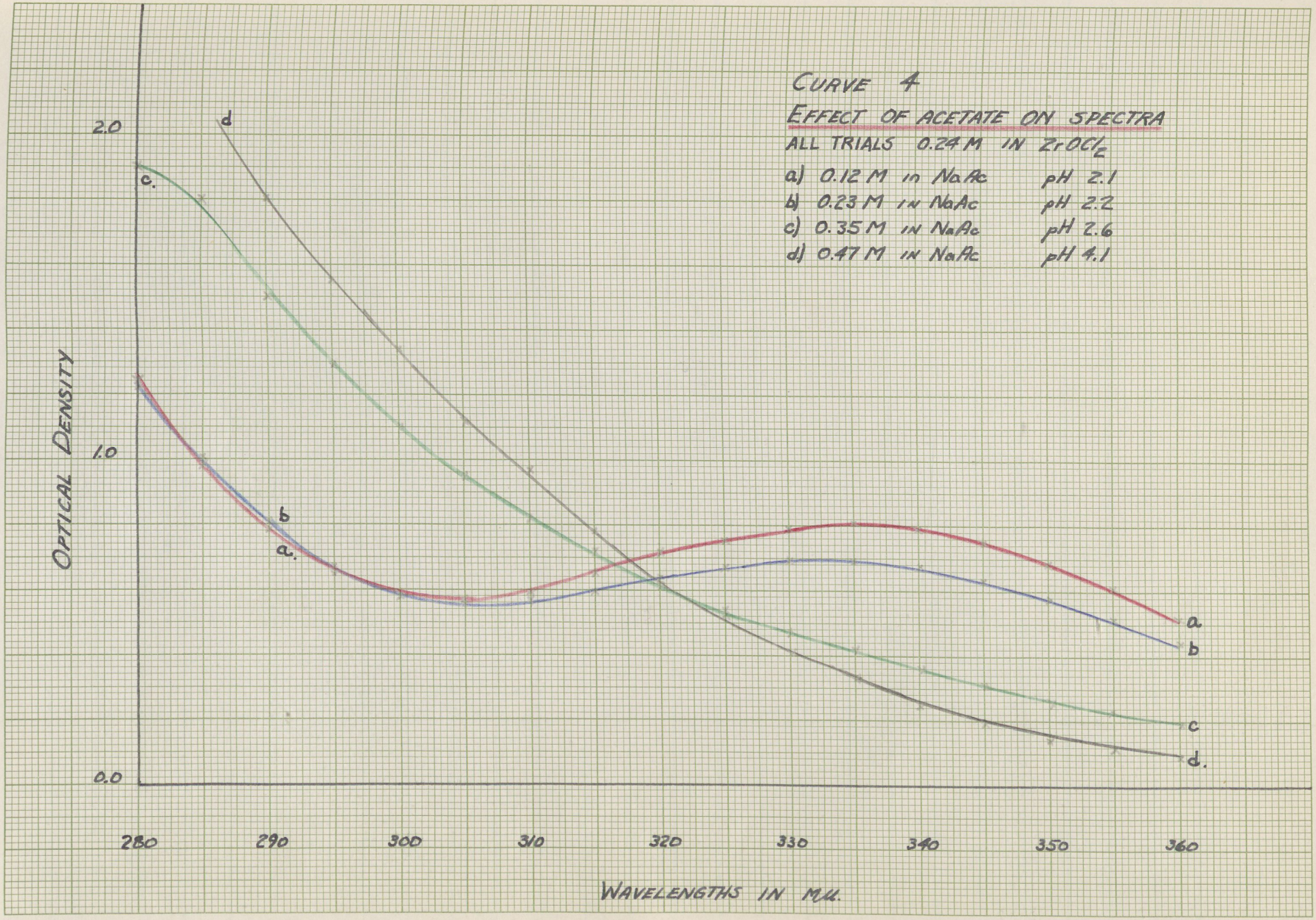
Spectra of Strong Acids

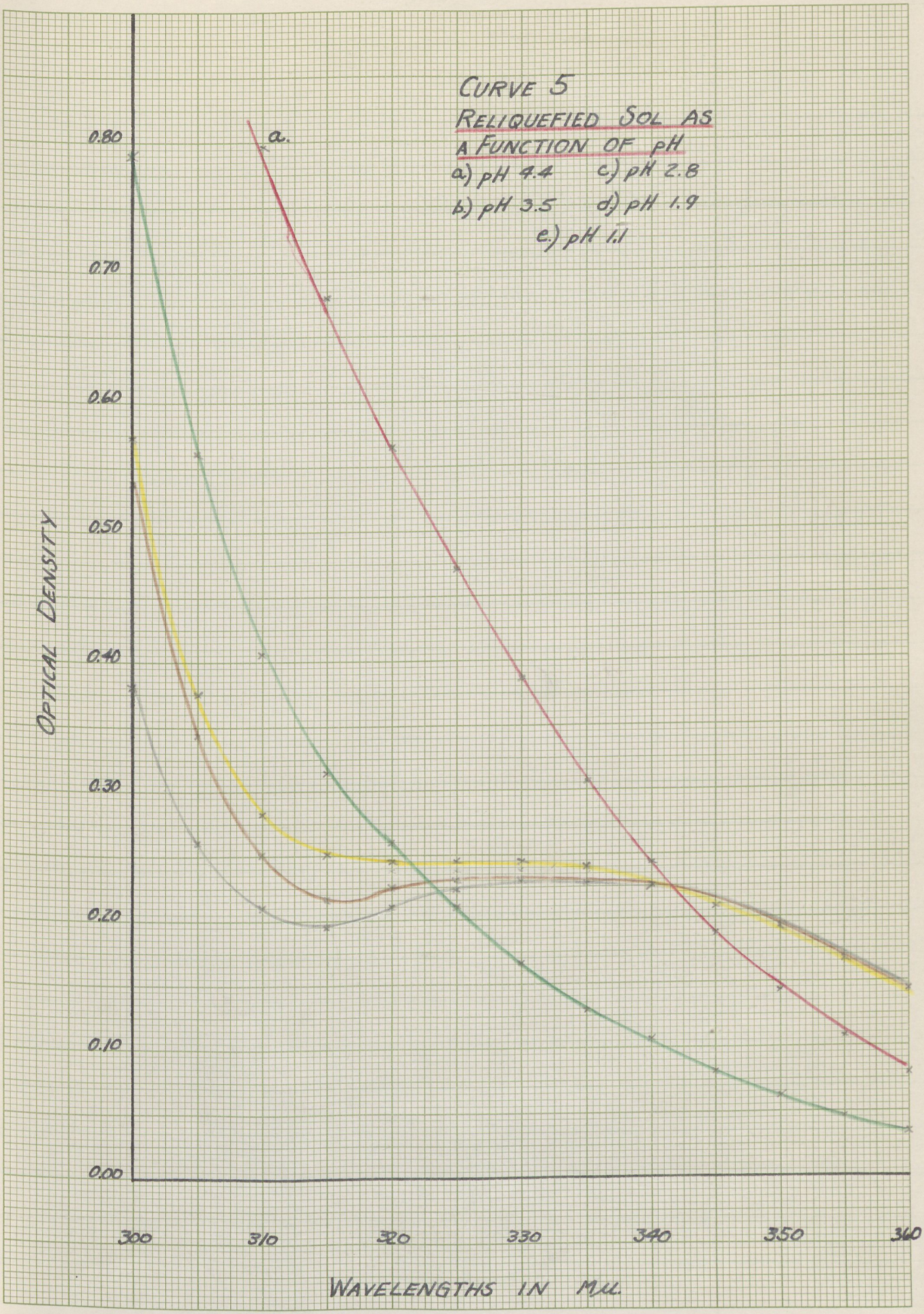
Wavelengths in mμ	Optical Density	
	Nitric Acid pH 1.1	Perchloric Acid pH 1.1
280	0.750	0.015
285	1.02	0.019
290	1.28	0.015
295	1.45	0.021
300	1.45	0.018
305	1.50	0.016
310	1.33	0.012
315	1.02	0.014
320	0.690	0.014
325	0.400	0.012
330	0.200	0.010
335	0.091	0.006
340	0.046	0.007
345	0.025	0.005
350	0.020	0.004

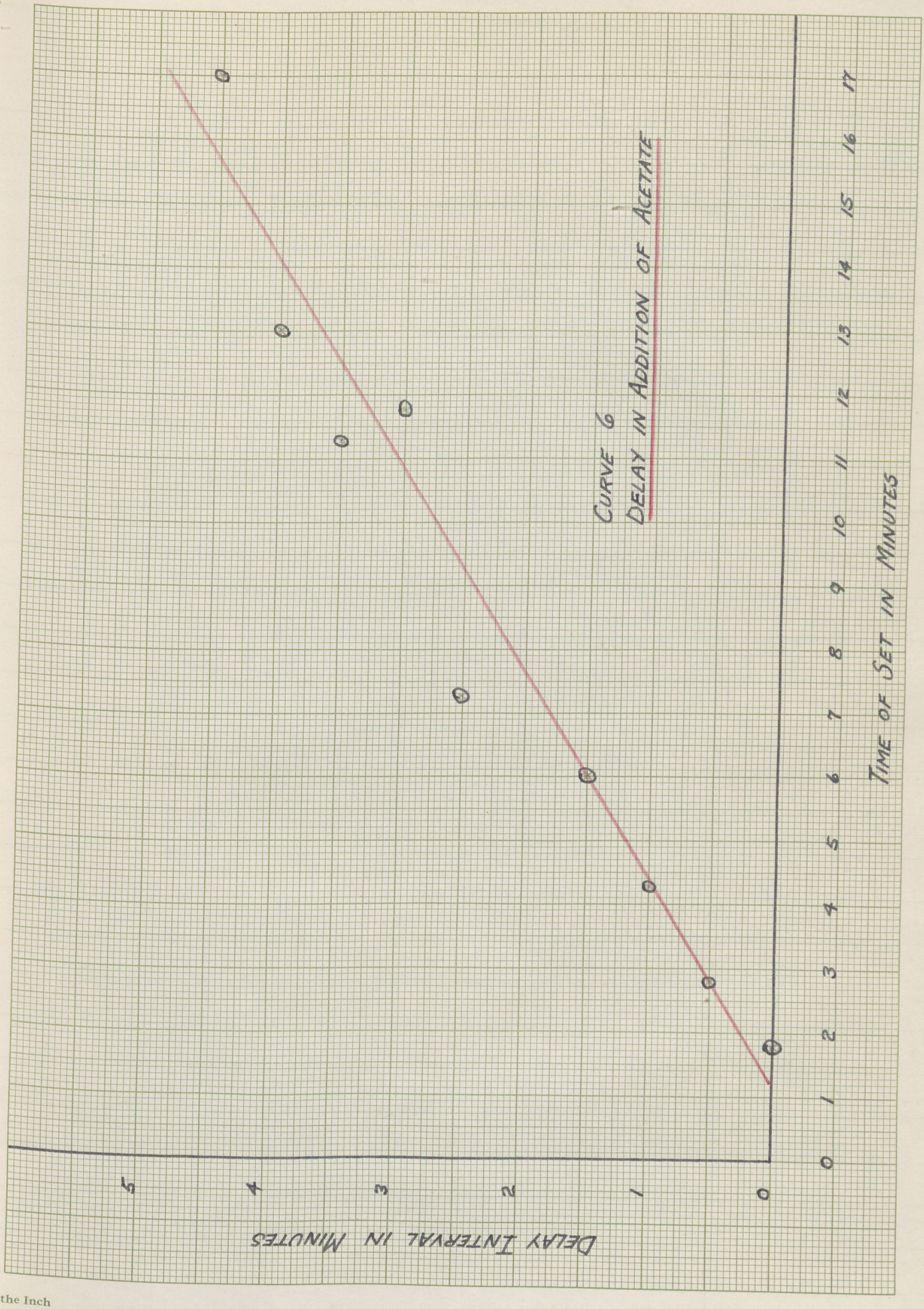

Time of Reliquefaction in hours (green)
2.0
1.5
1.1
Curve 1
Effect of Acetate
(after Hobday)
Milliliters 1.5 M. Sodium Acetate
30
28
26
24
22
20
18
16
14
pH
3.83
4.10
4.28
4.43
4.58
4.68
4.78
4.83
1.0
2.0
3.0
Time of Set in Minutes (red)

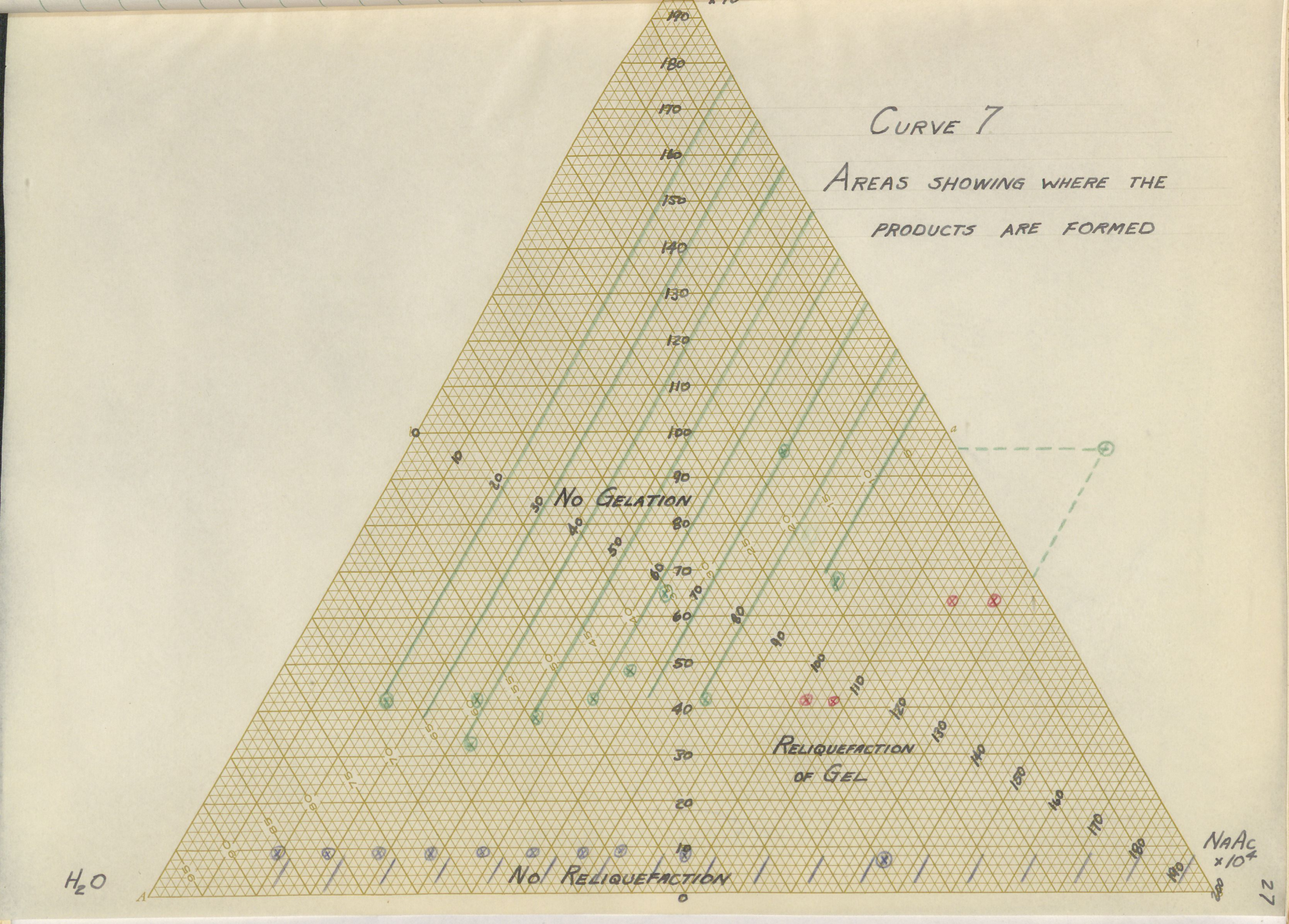

CURVE 2
SPECTRA OF REACTANTS
a.) 0.22 M. $ZrOCl_2$
b.) 1.2 M. $NaC_2H_3O_2$
c.) RELIQUEFIED SOL: 0.22M IN $ZrOCl_2$
1.2 M IN $NaC_2H_3O_2$
OPTICAL DENSITY
2.0
1.0
0.0
230
250
300
350
400
WAVELENGTHS IN MU


CURVE 3
EFFECT OF ACETIC ACID
a.) 0.07 M pH 1.6
b.) 0.21 M pH 1.1
c) 0.73 M pH 0.9
OPTICAL DENSITY
2.0
1.0
0.0
a.
b.
c.
c.
b.
a.
280
290
300
310
320
330
340
350
360
WAVELENGTHS IN MU.


CURVE 4
EFFECT OF ACETATE ON SPECTRA
ALL TRIALS 0.24 M IN $ZrOCl_2$
a) 0.12 M in NaAc pH 2.1
b) 0.23 M IN NaAc pH 2.2
c) 0.35 M IN NaAc pH 2.6
d) 0.47 M IN NaAc pH 4.1
OPTICAL DENSITY
2.0
1.0
0.0
280
290
300
310
320
330
340
350
360
WAVELENGTHS IN MU.
a
b
c
d


CURVE 5
RELIQUEFIED SOL AS A FUNCTION OF pH
a.) pH 4.4
b.) pH 3.5
c.) pH 2.8
d.) pH 1.9
e.) pH 1.1
a.
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
OPTICAL DENSITY
300
310
320
330
340
350
360
WAVELENGTHS IN MU.


Curve 6
Delay in Addition of Acetate
Time of Set in Minutes
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
Delay Interval in Minutes
0 1 2 3 4 5


CURVE 7
AREAS SHOWING WHERE THE
PRODUCTS ARE FORMED
No Gelation
Reliquefaction of Gel
No Reliquefaction
H2O
NaAc x10⁴
A
a
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
250
260
270
280
290
300
310
320
330
340
350
360
370
380
390
400
410
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870
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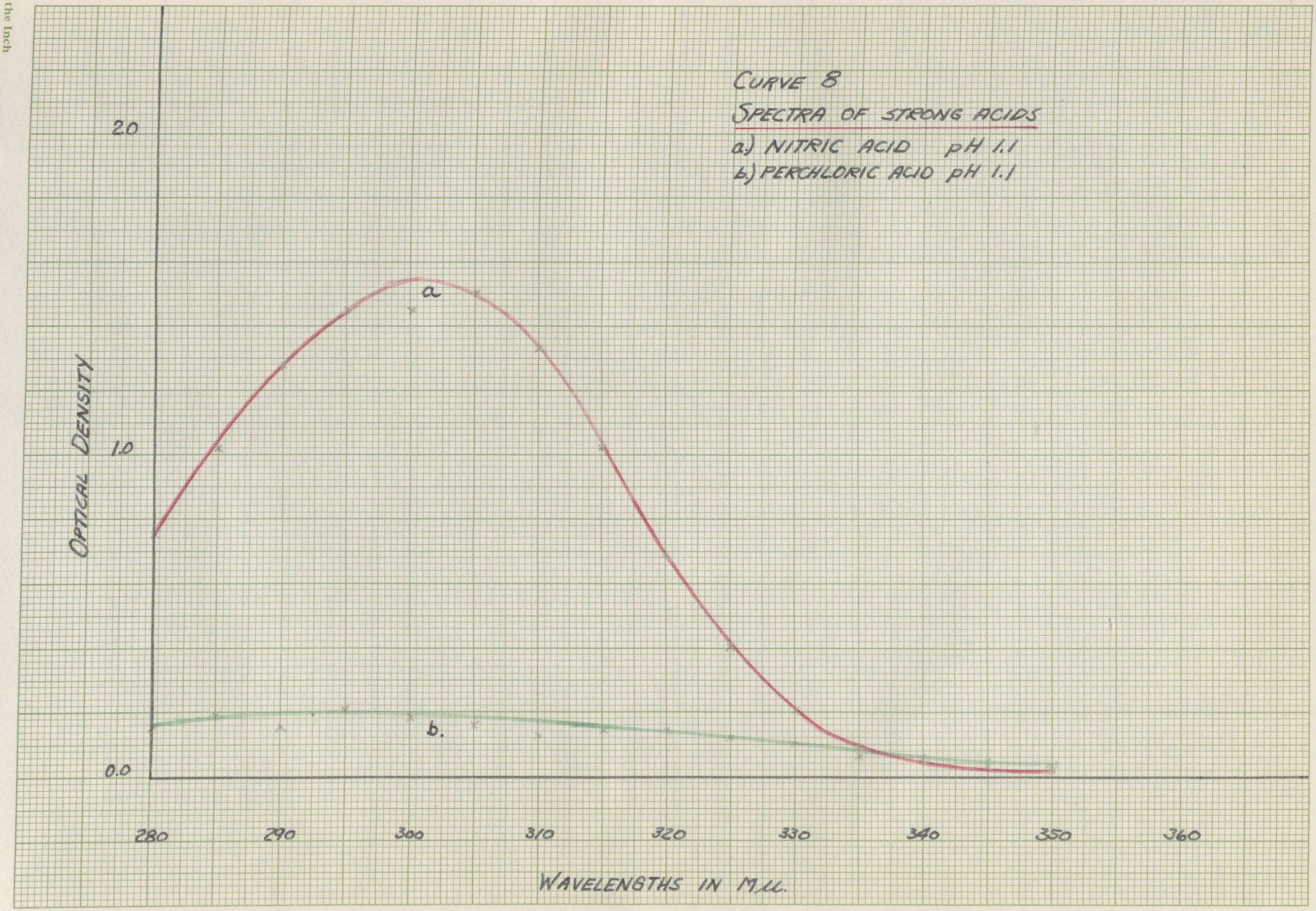
970
980
990
1000


CURVE 8
SPECTRA OF STRONG ACIDS
a.) NITRIC ACID pH 1.1
b.) PERCHLORIC ACID pH 1.1
2.0
1.0
0.0
OPTICAL DENSITY
a
b.
280
290
300
310
320
330
340
350
360
WAVELENGTHS IN MU.